

**ENVIRONMENTAL AND WASTE MANAGEMENT:
ADVANCES THROUGH THE ENVIRONMENTAL
MANAGEMENT SCIENCE PROGRAM**
Metal and DNAPL Contamination

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DIVISION OF ENVIRONMENTAL CHEMISTRY
227th American Chemical Society meeting
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Wednesday, March 31, 2004

Organizers: T. Zachry

Presiding: T. Ivory

Time	Paper
8:30 a.m.	Introductory Remarks.
8:35 a.m.	Novel methodology for metal ion separation based on molecular imprinting. <u>X. Zuo</u> , D. Mosha, M.M. Hassan, R.S. Givens and D.H. Busch
8:55 a.m.	Imprinted polymers in wastewater treatment. <u>C. Eastman</u> , S. Goodrich, I. Gartner and A. Mueller
9:15 a.m.	Phytoremediation of metal-contaminated soils. <u>I. Shtangeeva</u> , J. Laiho, H. Kahelin and G. Gobran
9:35 a.m.	Comparison of integrated AOP systems for BTEX removal from solution. <u>R.W. Peters</u> and J. Mohammad
9:55 a.m.	Transport, targeting and applications of metallic functional nanoparticles for degradation of DNAPL chlorinated organic solvents. <u>G.V. Lowry</u> , S. Majetich, D. Sholl, R.D. Tilton, K. Matyjaszewski, G.D. Redden, P. Meakin and H.W. Rollins
10:15 a.m.	Intermission.
10:35 a.m.	<i>In situ</i> chemical oxidation of contaminated ground water: Permanganate reactive barrier system for the long-term treatment of contaminants. <u>D. Li</u> and F. Schwartz

- 10:55 a.m. **Competitive sorption and desorption of chlorinated organic solvents (DNAPLs) in engineered natural organic matter.** J. Tang and W.J. Weber, Jr.
- 11:15 a.m. **Unique interfacial properties of the chlorinated solvent DNAPL at DOE's Savannah River Site.** S.E. Powers, K. Omrane and S.J. Grimberg
- 11:35 a.m. **Evaluation of the *in situ* aerobic cometabolism of chlorinated ethenes by toluene-utilizing microorganisms using push-pull tests.** M.F. Azizian, J. Istok and L. Semprini
- 11:55 a.m. Concluding Remarks.

ABSTRACTS

Novel methodology for metal ion separation based on molecular imprinting. Xiaobin Zuo, Donnati Mosha, Mansour M. Hassan, Richard S. Givens and Daryle H. Busch; Department of Chemistry, University of Kansas, 1251 Wescoe Hall Dr., Lawrence, KS 66045, Fax: 785-864-5747, xiaobinzuo@hotmail.com.

The siderophore-based extraction of iron from the soil by bacteria is proposed as a model for a new separation methodology labeled the soil poutice, a molecular device that would selectively retrieve the complex of a targeted metal ion. In this report we described the synthesis and characterization of molecularly imprinted polymers and their application in the specific recognition of macrocyclic metal complexes. The imprinting is based on non-covalent interactions such as hydrogen bonding, electrostatic attractions and minor metal-ligand coordination. Good rebinding capacity for the imprinting metal complex was observed in acetonitrile as well as in water. The polymers are resistant to strong acids and oxidizing agents and showed an increase of rebinding capacity during cycles of reuse. The imprinting procedure, combined with the previously known selective chelation of macrocyclic ligands, supports the feasibility of a new methodology that can be used to extract waste metal ions effectively and selectively from soils and ground water.

Imprinted polymers in wastewater treatment. Christopher Eastman¹, Scott Goodrich¹, Isabelle Gartner² and Anja Mueller¹; ¹Department of Chemistry, Clarkson University, Box # 5810, Potsdam, NY 13699, Fax: 315-268-6610, eastmacm@clarkson.edu; ²Department of Chemical Engineering, Virginia Polytechnic Institute and State University (Virginia Tech).

In wastewater treatment, a method that specifically recognizes a variety of impurities in a flexible manner would be useful for treatment facilities with varying needs. Current purification techniques (*i.e.* bacteria, oxidation, reduction, precipitation and filtration) are

nonspecific and difficult to control in complex mixtures. Heavy metal removal is particularly important in improving the efficiency of wastewater treatment, as they inhibit or even destroy the bacteria used for filtration. Imprinting polymerization is a technique that allows for the efficient removal of specific compounds and has been used in purification of enantiomers. It has potential to be applied in wastewater systems with the impurities acting as the template for the imprinting polymerization. The polymer with the bound impurities intact can then be removed *via* precipitation. After removal of the impurity the polymer can be reused. Data for the imprinting polymerization of polyacrylates and polyacrylamides for several metal complexes will be presented. Imprinting polymerization in combination with emulsion polymerization to improve the removal of hydrophobic contaminants will be described. Removal efficiencies will be presented and compared with conventional wastewater treatment methods.

Phytoremediation of metal-contaminated soils. Irina Shtangeeva¹, Jussi Laiho², Hanna Kahelin² and George Gobran³; ¹St. Petersburg University, St. Petersburg 199034, Russia, irina.shtangeeva@IS1179.spb.edu; ²Geological Survey of Finland; ³Department of Ecology and Environmental Research, Swedish University of Agricultural Sciences.

Recent concerns regarding environmental contamination have necessitated the development of appropriate technologies to assess the presence and mobility of metals in soil and estimate possible ways to decrease the level of soil metal contamination. Phytoremediation is an emerging technology that may be used to cleanup contaminated soils. Successful application of phytoremediation, however, depends upon various factors that must be carefully investigated and properly considered for specific site conditions. To efficiently affect the metal removal from contaminated soils we used the ability of plants to accumulate different metals and agricultural practices to improve soil quality and enhance plant biomass. Pot experiments were conducted to study metal transport through bulk soil to the rhizosphere and stimulate transfer of the metals to be more available for plants' form. The aim of the experimental study was also to find fertilizers that could enhance uptake of metals and their removal from contaminated soil.

Comparison of integrated AOP systems for BTEX removal from solution. Robert W. Peters and Jan Mohammad; Department of Civil and Environmental Engineering, University of Alabama at Birmingham, School of Engineering, 1075 13th Street South, Birmingham, AL 35294-4440, Fax: 205-934-9855, rpeters@eng.uab.edu.

This paper investigates the removal of BTEX compounds (benzene, toluene, ethylbenzene and xylene) from water using different advanced oxidation processes (AOPs) used singly or in combination with one another. This research is an extension of our work performed under the Environmental Management Science Program (EMSP) which addressed treating chlorinated organic contaminated water using sonication, vapor stripping and combined sonication + vapor stripping. In our current study, various

AOP processes were investigated for their ability to remove BTEX compounds from solution, including the following.

- ? Ultraviolet (UV) light alone
- ? UV light + hydrogen peroxide (H_2O_2)
- ? Sonication alone
- ? Air sparging alone
- ? Air sparging + sonication
- ? Air sparging + UV light
- ? Sonication + UV light
- ? Sonication + H_2O_2
- ? Sonication + air sparging + UV light
- ? Sonication + air sparging + H_2O_2
- ? Sonication + air sparging + H_2O_2 + UV light
- ? Sonication + air sparging with O_3
- ? Sonication + O_3 + H_2O_2
- ? Sonication + O_3 + H_2O_2 + UV light

Transport, targeting and applications of metallic functional nanoparticles for degradation of DNAPL chlorinated organic solvents. Gregory V. Lowry¹, Sara Majetich², David Sholl³, Robert D. Tilton⁴, Krzysztof Matyjaszewski⁵, George D. Redden⁶, Paul Meakin⁶ and Harry W. Rollins⁷; ¹Department of Civil & Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890, Fax: 412-268-7813, glowry@andrew.cmu.edu; ²Department of Physics, Carnegie Mellon University; ³Carnegie Mellon; ⁴Department of Chemical Engineering, Carnegie Mellon University; ⁵Department of Chemistry, Carnegie Mellon University; ⁶Idaho National Engineering and Environmental Laboratory; ⁷Chemistry Department, Idaho National Engineering and Environmental Laboratory.

Recently, laboratory and field studies have demonstrated that zero-valent iron nanoparticles (colloids) can rapidly transform dissolved chlorinated organic solvents into non-toxic compounds. This technology also has the potential to address Dense Non-Aqueous Phase Liquid (DNAPL) contamination, one of DOE's primary contamination problems. This project develops and tests polymer-modified reactive nanoscale Fe^0 particles for *in situ* delivery to chlorinated solvents that are present as DNAPLs in the subsurface. The surfaces of reactive Fe^0 -based nanoparticles are modified with amphiphilic block copolymers to maintain a stable suspension of the particles in water for transport in a porous matrix and to create an affinity for the water-DNAPL interface. Ultimately this will provide an improved technology to locate and eliminate DNAPL, a recalcitrant and persistent source for groundwater contamination by chlorinated solvents. Candidate polymers have been synthesized and attached to 20 nm SiO_2 particles using Atom Transfer Radical Polymerization (ATRP). The physical properties (hydrodynamic radius, stability, TCE-water partitioning behavior, mobility in a porous

matrix) of these nanostructures have been determined. The particles ($d_p \sim 102$ nm) are water soluble and partition to the TCE-water interface. The physical and chemical properties (e.g. oxide phase and thickness) of Fe^0 nanoparticles synthesized using different techniques and the effects of these properties on particle reactivity and efficiency have been evaluated. Numerical models (Brownian Dynamics) have been developed to predict the aqueous diffusivities of these particle-polymer nanostructures.

***In situ* chemical oxidation of contaminated ground water: Permanganate reactive barrier system for the long-term treatment of contaminants.** David Li and Frank Schwartz; Department of Geological Sciences, The Ohio State University, 225 Mendenhall Lab, 125 S. Oval Mall, Columbus, OH 43210, Fax: 614-292-7688, li@geology.ohio-state.edu.

Oxidation of chlorinated solvents by permanganate has proven to be effective in destroying these compounds in the aqueous phase. A semi-passive, well-based permanganate reactive barrier system (PRBS) was designed in order for the long-term treatment of dissolved contaminant in the ground water. Results from laboratory experiments indicate the PRBS could deliver permanganate at a stable, constant and controllable rate. In this paper, different field designs of the PRBS are discussed. Numerical simulation was conducted to elucidate the parameters that will influence the field implementation of a PRBS. We investigated issues such as permanganate consumption by aquifer materials, variable density flow effect, as well as lateral spreading under different geological settings. Results from this study continue to point to the promise of an *in situ* chemical oxidation scheme. PRBS provides a potential treatment of the contaminated ground water at relatively low management cost as compared with other alternatives.

Competitive sorption and desorption of chlorinated organic solvents (DNAPLs) in engineered natural organic matter. Jixin Tang¹ and Walter J. Weber, Jr.²; ¹Department of Civil and Environmental Engineering, University of Michigan, 2200 Bonisteel Blvd., 1211 ERB Building, Ann Arbor, MI 48109, jixin@umich.edu; ²Environmental and Water Resources Engineering, University of Michigan.

The effects of artificially accelerated geochemical condensation and maturation of natural organic matter on the sorption and desorption of trichloroethylene (TCE) and tetrachloroethylene (PCE) were studied. The sorption and desorption of TCE in the presence and absence of the competing PCE and 1,2-dichlorobenzene (DCB) were also examined. A sphagnum peat comprising geologically young organic matter was artificially “aged” using superheated water, thus increasing the aromaticity and the degree of condensation of its associated organic matter. The sorption of all solutes tested were increased remarkably and their respective desorptions reduced, by the aged peat. The sorption capacities and isotherm nonlinearities of the peat for both TCE and PCE were found to increase as treatment temperature increased. In the competitive sorption studies, both PCE and DCB were found to depress TCE sorption, with PCE

having greater effects than DCB, presumably because the molecular structure of the former is more similar to that of TCE.

Unique interfacial properties of the chlorinated solvent DNAPL at DOE's Savannah River Site. Susan E. Powers¹, Kamel Omrane² and Stefan J. Grimberg¹;

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Tetrachloroethene and trichloroethene are the primary constituents in a DNAPL found in the unsaturated zone at the Department of Energy's Savannah River Site (SRS). Following equilibration of the SRS DNAPL with deionized water, the measured interfacial tension was less than 2 dynes/cm and the pH of the aqueous phase 3.8, thus indicating the presence of constituents other than chlorinated solvents. Based on contamination history at DOE facilities, we explored the potential for co-contamination by oils, surfactants or organic acids. Non-aqueous potentiometric titration techniques revealed a high acid content (4 mg (as KOH)/g of DNAPL). Surrogate mixtures of TCE with the hydraulic oil, dibutylbutylphosphonate (DBBP) and tributylphosphate (TBP), which were used in the plutonium production process, also had low interfacial tension but not as low as the value measured for the SRS DNAPL. Research to identify the constituents and mechanisms responsible for the low interfacial tension of this DNAPL is on-going.

Evaluation of the *in situ* aerobic cometabolism of chlorinated ethenes by toluene-utilizing microorganisms using push-pull tests. Mohammad F. Azizian, Jonathan Istok and Lewis Semprini; Department of Civil, Construction and Environmental Engineering, Oregon State University, Corvallis, OR 97331, mohammad.azizian@orst.edu.

Single-well-push-pull tests were used in a contaminated aquifer to evaluate the ability of toluene-oxidizing microorganisms to aerobically cometabolize chlorinated aliphatic hydrocarbons (CAHs) such as trichloroethene (TCE). Groundwater containing dissolved toluene was injected into the saturated zone in biostimulate indigenous toluene-utilizers. The test solution was injected into the aquifer using a standard monitoring well and then was transported under natural-gradient conditions. Transport tests demonstrated similar transport characteristics of the conservative tracer and the reactive solutes. Biostimulation tests were then performed by injecting a test solution containing dissolved toluene substrate, hydrogen peroxide, bromide and nitrate in order to increase the biomass of toluene-utilizing microorganisms. During the biostimulation tests, decreases in toluene concentration and the production of *o*-cresol as an intermediate oxidation product, indicated the simulation of toluene-utilizing microorganisms containing an *ortho*-monooxygenase enzyme. Transformation tests conducted after biostimulation demonstrated that indigenous microorganisms have the capability to

transform the surrogate compounds (e.g. isobutene). Isobutene was transformed to isobutene oxide, indicating transformation by a toluene *ortho*-monooxygenase.